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Production of Nitric Oxide in the Pyrolysis of Aromatic Nitro Compounds

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The pyrolysis of nitrobenzene in the temperature range 400–600 °C was studied in a continuous-flow apparatus consisting of pyrolyzer, gas chromatograph, and mass spectrometer. Several of the observed products (benzene, biphenyl, naphthalene) could arise from phenyl radical, but, in contrast to earlier suggestions, there is no evidence supporting a primary fission to phenyl radical and nitrogen dioxide. Pyrolysis of nitrosobenzene yields products similar to those from nitrobenzene, and a two-step mechanism, nitrobenzene → nitrosobenzene → phenyl, is proposed. Although the details of the mechanism are not conclusively proven, there is considerable evidence for a heterogeneous mechanism and none supporting a homogeneous mechanism.

Recent experience in this laboratory¹ and others² has shown that nitric oxide is a prominent product of the pyrolysis of aromatic nitro compounds, and that nitrogen dioxide is not produced in detectable quantities. This is not necessarily a surprising result inasmuch as the possible rearrangement to

an aryl nitrite leads to compounds which should readily undergo homolytic fission to nitric oxide plus aryloxy radicals. Photochemical nitro–nitrite rearrangements are known,³ and the analogous rearrangement of the positive ion occurs in the mass spectrum of nitrobenzene.⁴ Even though there is little

evidence that such a process takes place by thermal stimulus at ordinary temperatures, it is quite possible that it occurs readily at high temperature.

The bond dissociation energy corresponding to the homolytic fission of phenyl nitrite into nitric oxide and phenoxy radicals is 23.7 kcal/mol.⁵ By comparison, the homolytic fission of an aromatic nitro compound to an aryl radical and NO₂ should be less favorable; a lower limit to $D(\text{PhNO}_2)$ of 63 ± 3 kcal may be estimated from the heats of formation of phenyl radical,⁶ NO₂, and nitrobenzene.⁷ Thus, if the nitro-nitrite rearrangement is not a rapid one, the production of NO₂ should compete favorably with the production of NO in the pyrolysis of nitrobenzene, and by extension, of other aromatic nitro compounds as well. If on the other hand the thermal nitro-nitrite rearrangement is a facile one, little, if any, NO₂ would be expected in the pyrolysis of an aromatic nitro compound.

Several recent publications^{2,8,9} concern the pyrolysis of nitrobenzene in a packed-tube reactor at 600 °C. The products of pyrolysis under these conditions were explained on the basis of primary fission of the C-N bond, yielding phenyl radical and nitrogen dioxide. However, as in our experience, no NO₂ was observed in the reactor effluent. The available evidence does not, therefore, favor primary C-N fission over other possibilities for the formation of phenyl radical.

Experimental Section

Nitrogen dioxide was purchased from Matheson, and subjected to several freeze-thaw cycles at -78 °C before use. Nitrobenzene and nitrosobenzene (reagent grade) were purchased from Eastman, and used as received. Samples to be pyrolyzed were injected into a Fisher-Victoreen pyrolyzer, and passed directly into a gas chromatograph and thence into the ion source of a Bendix MA-2 time-of-flight mass spectrometer.

In the Fisher-Victoreen instrument the pyrolysis chamber is a straight stainless steel tube of 0.6 cm i.d. and length 10 cm; the tube is rapidly (<1 s) raised from room temperature to a preselected pyrolysis temperature by resistive heating and held there for a preselected time. In our experiments that hold time always exceeded the reactor residence time (~20 s). Samples were either directly injected through a rubber septum, or else introduced via small stainless steel boats inserted into the reactor. All connecting tubing was maintained at a temperature (100 °C) insufficient for pyrolysis, as shown by blank runs. The GC column was stainless steel, 6 ft \times 0.125 in., 10% SE-30 on Chromosorb W, or in some experiments, a dummy column (10 ft \times 0.125 in. stainless steel tubing, no packing). Helium carrier gas was used at a flow rate of 10 ml/min.

The quantity to be determined in most experiments was the amount of NO₂ produced in pyrolyses. Monitoring of the mass spectral intensity at m/e 46 is not an adequate test for the presence of trace quantities of NO₂; CO₂, which is produced in the pyrolyses and/or present as impurity or background, also has a peak (isotopic) at m/e 46. The natural abundance of ¹⁸O is such that, in the mass spectrum of pure CO₂, the ratio I_{46}/I_{44} should be close to 4×10^{-3} .

The mass spectrometer was therefore arranged for simultaneous monitoring of the intensities at m/e 44 and 46, and any increase of the ratio $R = I_{46}/I_{44}$ from the value obtained from a sample of pure CO₂ was taken as evidence of the presence of NO₂. Several calibration runs with pure CO₂ were made before each nitrobenzene pyrolysis in order to establish the relative instrumental response factors for the two output channels; the relative sensitivities were such that for pure CO₂ $I_{46}/I_{44} = 3.7 \times 10^{-3}$.

Results

Loss of NO₂ in the Column and Pyrolyzer. Preliminary runs were made to determine whether NO₂, if produced in pyrolyses, would survive the journey to the mass spectrometer ion source. Several 10- μ l samples of NO₂/N₂O₄ at atmospheric pressure were injected into the pyrolyzer, which in these experiments was held at room temperature. The results were uniform and unambiguous: NO₂ is completely consumed, and large quantities of NO appear during the ca. 1.5-min journey through the SE-30 column at 100 °C. Conversely, when the packed column was replaced with the dummy column and no

other element of apparatus or procedure was changed, large amounts of NO₂ survived. Little, if any, NO was formed under these conditions: the peak heights at m/e 46 and 30 were in proportion appropriate to the mass spectrum of pure NO₂, but the reliability of this type of measurement is such that up to perhaps 10% of the original NO₂ could have been converted to NO. In any case, it is clear that NO₂ survives the dummy column but not the packed column.

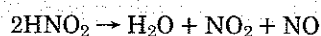
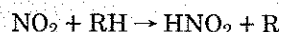
The possibility that NO₂ is consumed in the pyrolyzer itself was also checked, by the introduction of several 10- μ l samples of NO₂ into the pyrolyzer at 400 °C; the dummy column was used for these runs. The results of five determinations were $0.002 < R < 0.004$, showing clearly that NO₂ is entirely consumed. (That R is in fact less than that expected for CO₂ may be due to the presence of some N₂O, for which $R = 0.002$. However since these results were obtained from rather small peak heights, the results should not be taken to prove the presence of N₂O.) Similar determinations with the same sample and the pyrolyzer at room temperature gave $500 < R < 1700$, showing that NO₂ survives.

These observations could be explained if carbonaceous deposits from previous pyrolyses of organic samples remained in the pyrolyzer and thus provided an efficient surface for the heterogeneous reduction of NO₂, e.g., $\text{C} + \text{NO}_2 \rightarrow \text{CO} + \text{NO}$. Accordingly the surface was treated with pure oxygen flowing at ca. 60 ml/min through the pyrolyzer, held at 600 °C. This treatment was continued for 0.5 h, and produced a marked effect on NO₂ survival.

When several 10- μ l samples of NO₂ were injected into the oxygenated pyrolyzer at 400 °C, values of R were obtained which were greater by 3-4 orders of magnitude than the values obtained with the unoxygenated pyrolyzer. The R values varied, probably owing to varying amounts of CO₂ in the NO₂ sample,¹⁰ and/or variable surface effects. On the two different days this experiment was carried out, average values of 2.5 and 2.0 were obtained. Control experiments with the pyrolyzer at room temperature yielded values of 4.3 and 7.3 on two different days. Apparently some NO₂ is destroyed at higher temperatures, but for the most part it survives. Similar experiments with the pyrolyzer at 500 °C yielded lesser values of R (~1.0) showing increasing NO₂ destruction as the pyrolyzer temperature is raised. Subsequent NO₂ determinations were therefore done only at 400 °C, a temperature sufficiently great for pyrolysis but not so high as to cause complete destruction of NO₂.

Pyrolysis of Nitrobenzene. When 0.1- μ l samples of neat nitrobenzene were injected into the pyrolyzer at 400 °C two distinct results were obtained, depending on the temperature of the dummy column. If the column was at 125 °C, all material was eluted in a single peak, which showed a 46/44 ratio of about 0.7. If the dummy column temperature was 50 °C, some separation took place and three peaks were eluted. These are (1), CO₂, NO, and benzene; (2), nitrosobenzene; and (3), unpyrolyzed nitrobenzene. Any NO₂ present would be eluted with the CO₂/NO/C₆H₆ fraction. The value of R obtained for this fraction in four separate determinations was in the range 0.002-0.004. That is, no NO₂ was observed.

It has been suggested⁸ that NO₂ is produced in pyrolyses, but is converted to NO via a nitrous acid mechanism:



where the H-atom donor in the first step is primarily nitrobenzene itself. In the present work this possibility was checked by the 400 °C pyrolysis of a mixture of NO₂ (4×10^{-7} mol) and nitrobenzene (10^{-5} mol), under conditions such that the NO₂ and nitrobenzene fractions were well separated by the dummy column. The resulting intensity ratio 46/44 of 7.8 indicates

Table I. Products of Nitrobenzene Pyrolysis

Product	Pyrolysis temp, °C				
	400	450	500	550	600
NO ₂ + NO ^a	0.7 ^b (0.8)	0.8 (0.7)	2.9 (2.4)	7.5 (6.9)	14.8 (19.0)
Benzene	0.3 (0.03)	0.6 (0.2)	1.9 (1.6)	7.0 (5.5)	15.5 (14.8)
Nitrosobenzene	3.1 (1.3)	2.2 (0.3)	(0.2)	0.08 (0.03)	0.2 (<0.5)
Aniline	9.6 (0.03)	4.1 (0.5)	7.0 (3.1)	12.2 (7.5)	15.1 (17.9)
Nitrobenzene	86.3 (93.6)	92.3 (94.7)	74.6 (84.4)	44.3 (57.5)	14.5 (7.4)
Naphthalene			(0.4)	1.6 (1.1)	4.3 (4.0)
Biphenyl + phenyl ether ^a	(1.7)	(1.0)	3.5 (2.9)	6.3 (5.1)	10.8 (9.7)
Dibenzofuran	(2.5)	(0.8)	3.8 (2.6)	6.5 (6.0)	10.5 (9.8)

^a Not separated under these chromatographic conditions. ^b Percentage of the total integrated area of the chromatogram. Numbers in parentheses are the results of a repeated determination.

that much of the NO₂ survived in spite of the 25-fold excess of nitrobenzene. Thus the above mechanism cannot explain the absence of NO₂ in pure nitrobenzene pyrolyses.

Products of Nitrobenzene Pyrolysis. Several pyrolyses of 0.1 μ l of nitrobenzene were carried out with the SE-30 column rather than the dummy, in order to identify and measure the products. The column was temperature programmed for 2 min at 70 °C, then 25 °C/min to 240 °C, with a helium flow rate of 20 ml/min. Under these conditions the residence time in the reactor was about 10 s. Quantitative analysis was obtained by digital integration of the GC peak areas, using the mass spectrometer total ion current monitor as the detector. These results are collected in Table I. Not shown in Table I is some high molecular weight material formed in amounts too small for mass spectral identification.

Discussion

Several points should be made in regard to the results in Table I. In the first place, the extent of agreement between the results of repeated determinations indicates that attention should be focussed on general trends rather than on numerical results. Lack of precise agreement is expected if there is a variable heterogeneous contribution to the pyrolysis mechanism, and we have already demonstrated a variable heterogeneous effect on NO₂ consumption (reactor oxygenation experiments, *vide supra*).

The lack of reproducibility of product distribution is more striking and significant when the results of previous investigations are considered. For example, in nitrobenzene pyrolysis at 700 °C, Patterson et al.⁹ found the ratio of dibenzofuran to aniline among the products to be 83:1; the same ratio observed by Fields and Myerson² at 600 °C was 11:1 and in this work at 600 °C, 0.8:1. In both the other laboratories the pyrolysis chamber was quartz or Vycor, whereas in our experiments it was stainless steel. Secondly, the relatively large amount of aniline formed at all temperatures in the present work also indicates a significant heterogeneous contribution, since this product could hardly be formed via a homogeneous mechanism.

It is interesting that the results from three laboratories are in much better agreement when the dibenzofuran-biphenyl ratios are considered, since both these compounds could be formed homogeneously. Patterson et al. found 0.85:1, Fields and Myerson found 0.75:1, and we found 0.97:1.

Thirdly, the behavior of nitrosobenzene is unique: it alone is produced to a decreasing extent as the reaction temperature is increased. When this fact is considered together with our finding that NO₂ is not produced in significant quantities, it lends support to the hypothesis that the mechanism of nitrobenzene pyrolysis involves a nitrosobenzene intermediate rather than the direct cleavage to NO₂ and phenyl radical.

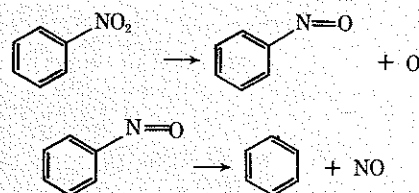
In order to confirm the hypothesis of the intermediacy of

nitrosobenzene, several experiments were performed in which nitrosobenzene itself was pyrolyzed. These experiments differed from the nitrobenzene pyrolyses in that the sample, solid at room temperature, was dissolved in benzene (~170 mg of nitrosobenzene/ml benzene); 0.3 μ l of the solution was then injected into the pyrolyzer. Thus there was present in the nitrosobenzene pyrolyses a larger amount of benzene than in the case of nitrobenzene pyrolysis. A second difference was that much lower temperatures sufficed for nitrosobenzene pyrolysis, as might be expected from the behavior of the nitrosobenzene produced in nitrobenzene pyrolyses.

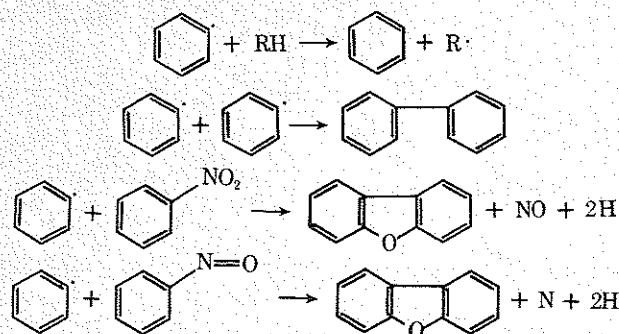
The results of these experiments were striking in their similarity to nitrobenzene pyrolysis, and lend strong support to the hypothesis of nitrosobenzene intermediacy. In the pyrolysis of nitrosobenzene (in benzene solution) at 275 °C the products were CO₂ + NO (3.4), benzene (62.9), nitrosobenzene (8.4), aniline + phenol (3.1), nitrobenzene (1.9), naphthalene (trace), biphenyl (6.7), dibenzofuran (1.7), and hydroxyphenylbenzene (3.9). The numbers in parentheses give the percentage of the total integrated area of the chromatogram. Also, the identification of hydroxyphenylbenzene is probable rather than certain, since it is not confirmed by comparison with literature or authentic sample spectra. As in the case of nitrobenzene pyrolysis, some high molecular weight material was formed, in amounts insufficient for mass spectral identification.

Conclusion

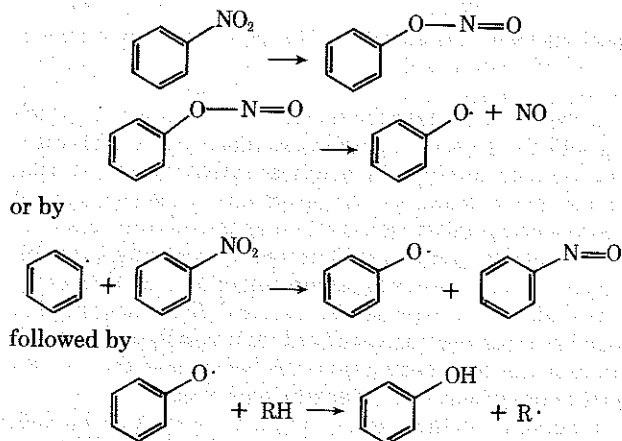
We propose that the initial phase of nitrobenzene pyrolysis is the formation of phenyl radical via the intermediate formation of nitrosobenzene:



The major products benzene, biphenyl, and dibenzofuran are the expected products of phenyl radical reactions:



The major difference between this mechanism and that proposed by Fields and Meyerson⁸ is that we do not postulate as a primary step the direct fission of nitrobenzene to NO_2 and phenyl radical, a step which, in our view, is not supported by the evidence. Also, in our experiments phenol was not observed as a product of nitrobenzene pyrolysis under any circumstances, whereas Fields and Meyerson reported phenol as the most prominent product at 600 °C. This again supports the conclusion that heterogeneous processes are of great importance in pyrolyses of aromatic nitro compounds. Formation of phenolic products most probably involves the prior production of phenoxy radical, either by



without specifying whether these are homo- or heterogeneous processes.

As we have stressed, surface reactions play a dominant role in pyrolyses. It might therefore be asked, what is the evidence for a *homogeneous* mechanism. The answer, considering both present and previous results, is that even though many of the reactions discussed above could proceed as uni- or bimolecular gas phase reactions, there is *no* evidence that nitrobenzene pyrolysis takes place to any extent by a homogeneous mechanism.

Registry No.—Nitric oxide, 10102-44-0; nitrobenzene, 98-95-3.

References and Notes

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- (10) The NO_2 was stored in a flask equipped with a rubber septum, which after a time was degraded by the NO_2 , with the resulting production of CO_2 . As described above, our test for NO_2 was not affected by the presence of CO_2 , even in relatively large amounts.